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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification⁵ : C08J 3/00, C08K 3/22, 9/00 C08L 33/00, 51/00, 41/00 C08L 31/00	A1	(11) International Publication Number: WO 93/11181 (43) International Publication Date: 10 June 1993 (10.06.93)
(21) International Application Number: PCT/US92/09434 (22) International Filing Date: 4 November 1992 (04.11.92) (30) Priority data: 801,976 3 December 1991 (03.12.91) US (60) Parent Application or Grant (63) Related by Continuation US 801,976 (CON) Filed on 3 December 1991 (03.12.91) (71)(72) Applicants and Inventors: EMMONS, William, D. [US/ US]; 1411 Holcombe Road, Huntingdon Valley, PA 19006 (US). VOGEL, Martin [US/US]; 550 Pine Tree Road, Jenkintown, PA 19046 (US). KOSTANSEK, Ed- ward, C. [US/US]; 2425 Durham Road, Buckingham, PA 18912 (US). THIBEAULT, Jack, C. [US/US]; 10-1 Aspen Way, Doylestown, PA 18901 (US). SPERRY, Pe- ter, R. [US/US]; 49 Woodview Drive, Doylestown, PA 18901 (US).		(74) Agents: SLUZAS, Alex, R. et al.; Paul & Paul, 2900 Two Thousand Market Street, Philadelphia, PA 19103 (US). (81) Designated States: AT, AU, BR, CH, DE, DK, ES, FI, GB, HU, JP, LU, NL, NO, SE, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, SE). Published <i>With international search report.</i>
(54) Title: PROCESS FOR PREPARING AN AQUEOUS DISPERSION INCLUDING POLYMERIC LATEX AND TITA- NIUM DIOXIDE PIGMENT (57) Abstract Titanium dioxide pigment particles are dispersed in an aqueous medium. A selected, relatively hard, polymeric latex is added, as well as a film-forming binder to give a formulated coating composition. The selected polymeric latex can include residues of polymerized dihydrogen phosphate functional groups, or have a high level of acid functional groups or greater than one percent itaconic acid. The selected latex particles improve the opacity of the coating film. Alternatively, a single selected polymeric latex is used to both improve opacity and to serve as binder, or a mixture of a selected polymeric latex having a low effective glass transition temperature and a conventional binder latex is employed.		

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**PROCESS FOR PREPARING AN AQUEOUS DISPERSION INCLUDING
POLYMERIC LATEX AND TITANIUM DIOXIDE PIGMENT**

BACKGROUND OF THE INVENTION

1. Field Of The Invention

This invention relates generally to a process for preparing aqueous compositions including polymeric latex and titanium dioxide pigment, and more particularly to the opacity of products formed by the loss of water from such aqueous compositions.

2. Background Of The Invention

Aqueous dispersions of polymeric latex are used to prepare a tremendous variety of commercially important products, including paints, coatings, primers, and inks. Frequently, the polymeric latex is included to form a continuous phase as the water is lost in order to bind the product together, and to contribute important physical properties. In addition to the polymeric latex, most products include particles of one or more inorganic materials. Some inorganic materials contribute an important functional property to the product, such as opacity or color.

Titanium dioxide has been for many years the pigment of choice for conferring opacity to plastic sheets and films, and particularly to coatings formed from coating compositions and paints. In paints titanium dioxide is typically the most expensive component of the formulation. It has been an ongoing objective of the coatings industry to achieve the desired degree of opacity in a coating while at the same time using as little titanium dioxide pigment as possible.

In the case of latex paints and coatings, it is conventional practice to first form a stable aqueous dispersion of titanium dioxide pigment with other fillers or

extenders. This dispersion, also known as a "mill base" or "grind," may contain water-miscible solvents, such as for example glycols and glycol ethers, and relatively low molecular weight water soluble polyelectrolytes as titanium dioxide pigment grinding aids or dispersants. Common practice is to form a stable dispersion of titanium dioxide pigment, and then to add to the dispersion the aqueous latex polymer binder along with the other ingredients, such as for example thickeners and rheology modifiers, antifoaming agents, colorants, coalescing agents or temporary plasticizers for the latex polymer particles, and surfactants for substrate wetting and colorant compatibility. This process is discussed further in T.C. Patton, Paint Flow and Pigment Dispersion (Wiley Interscience, 2nd edition) 290-295 (1979); Treatise on Coatings, Vol. III, Part 1 (Marcel Decker) (1975); Pigment Handbook, Vol. I (2nd edition, Wiley Interscience) (1988), and Pigment Handbook, Vol. III (Wiley Interscience) (1973).

There is a continuing need to improve the effective utilization of titanium dioxide in aqueous coating compositions and thereby to improve the opacity and other performance properties of coating compositions.

SUMMARY OF THE INVENTION

The present invention provides a process for preparing an aqueous dispersion including selected polymeric latex particles and titanium dioxide pigment particles for use in preparing formulate aqueous compositions, such as coating compositions, paints, and inks, which in turn give coatings which show improved opacity compared to prior art formulations.

The process of the present invention contemplates dispersing titanium dioxide pigment particles in an aqueous medium with a pigment dispersant, such as a polyelectrolyte pigment dispersant. The process of this invention further

contemplates preparing a dispersion or suspension of selected polymeric latex particles in the aqueous medium.

The selected polymeric latex particles can be prepared by processes which are believed to provide
5 water-insoluble polymer latexes with a high level of acid-functional monomer, processes which provide polymeric latexes with more than one percent itaconic acid, or processes which provide copolymerization of dihydrogen phosphate-functional monomers.

10 In addition to the selected polymeric latex, other components can be added depending on the application for the aqueous composition. For example, a film-forming binder such as a relatively soft polymeric latex can be included, as well as other conventional components used to provide a
15 formulated coating composition, such as coalescents, preservatives, thickeners, and rheology control agents.

Preferably, the selected polymeric latex particles are polymerized from monomer which provides polymer which is hard or rigid at the temperature at which the aqueous
20 composition is to be used, such as monomer which provides a polymeric material with an effective glass transition temperature of at least about 20°C, more preferably at least about 35 °C, and even more preferably at least about 50 °C in the case of a composition applied at ambient or room
25 temperature (that is, at about 20 - 23 °C). Higher temperature ranges may be more appropriate for applications at higher temperatures, such as baked coatings.

Alternatively, the selected polymeric latex can have a low effective glass transition temperature and serve as a
30 binder for the composition.

The improved opacity provided by the present invention advantageously provides greater flexibility in preparing aqueous compositions including polymeric latex and dispersed titanium dioxide pigment. For example, in some
35 cases the present process provides a means of reducing the amount of titanium dioxide pigment required to provide the

desired opacification. When the selected polymeric latex is used in coating compositions, the present process provides improved coating properties, such as opacity or hiding, tint strength, mechanical properties, "ICI" or "cone-and-plate" (high shear rate) viscosity, gloss, and scrub resistance. The process also provides coating compositions giving coatings with improved opacity for a given titanium dioxide pigment level.

The selected polymeric latex particles resulting from the process of this invention are particularly useful for improving the performance properties and permeability of coatings and paints formed therefrom. Alternatively, the process of the invention offers the ability to formulate coatings and films of substantially equal performance properties as conventional systems but with lower concentrations of expensive titanium dioxide pigment, and accordingly at lower cost. The process of the present invention further contemplates preparing fully formulated aqueous compositions, including aqueous coating compositions, using the selected polymeric latex particles, and the subsequent use of the fully formulated aqueous compositions to form products, including coatings, and coated articles.

In one presently preferred embodiment, the process of this invention contemplates preparing a mixture of at least two types of polymeric latex particles, the first type being the selected polymeric latex particles, and preferably having an effective glass transition temperature of at least about 20 °C, more preferably at least about 35 °C, and even more preferably at least about 50 °C. The second type of polymeric latex particle is provided to form a binder for the titanium dioxide pigment particles. The mixture can be used to prepare formulated compositions, such as coating compositions, which show improved opacity.

In another preferred embodiment, two or more types of soft polymeric particles are employed as binders, one or

more of these being the selected polymer latex.

DETAILED DESCRIPTION

5 The process of the present invention provides selected polymeric latexes for use in aqueous compositions including titanium dioxide pigment particles, the titanium dioxide pigment particles having been initially dispersed
10 using a pigment dispersant, such as a polyelectrolyte dispersant, or a stearic stabilization agent.

 The process provides a solution to the problem of how to practically utilize polymeric latex particles to improve the opacity of aqueous-based coatings containing high
15 concentrations of titanium dioxide pigment particles.

 Polymeric latex particles of selected composition and size can be effectively used in the process of the present invention along with titanium dioxide particles, in concentrated dispersions.

20 In one presently preferred embodiment, a water-insoluble polymeric latex is polymerized from monomer mixture including a high level, such as at least about ten percent by weight of polymer solids, of carboxylic acid-functional monomer. In another presently preferred
25 embodiment, a polymeric latex prepared from monomer including more than one percent by weight itaconic acid is employed. In still another presently preferred embodiment, a polymeric latex prepared from monomer including at least one polymerizable ethylenically unsaturated dihydrogen
30 phosphate ester, such as a dihydrogen phosphate ester of 2-hydroxyethyl methacrylate, is employed.

 The present process is particularly useful for improving the opacity, gloss, high shear viscosity, color development, permeability, and mechanical properties of
35 coatings and films formed therefrom. Alternatively, the invention offers the ability to formulate coatings and films of substantially equal performance properties as conventional systems but with lower titanium dioxide pigment

particle concentrations and accordingly at lower cost.

The entire accessible pH scale is useful in the practice of this invention although it is preferred for reasons of excessive particle solubility, corrosion both to
5 substrates and to the skin, and the like, to restrict the range to approximately 2 to 12 and more preferably in the range of from about 4 to about 10.

Titanium dioxide particles which have been subjected to prior surface treatment processes can be used in the
10 process of the present invention. For example, titanium dioxide is available with various types of prior surface treatments which provide surface coatings of alumina or silica or mixtures of both, as discussed in A. Brisson et al., J. Coatings Tech. 63 59 - 65 (1991).

15 The process of the present invention is believed to be dependent to some extent on the relative concentrations of the selected polymeric latex particles and the titanium dioxide pigment particles with larger polymeric latex particles being required at a higher concentration for
20 optimum performance. Preferably, enough of the selected polymeric latex is employed to obtain optimum performance properties in fully formulated products prepared using the process.

In preparing coating formulations possessing
25 desirable performance properties it is not necessary that the selected polymeric latex used in the process of the invention to also function as the polymeric binder for the coating or film, although this may be possible or even desirable in some cases. Instead, another polymeric latex
30 material, preferably having a glass transition temperature tending to provide good film formation properties under the application conditions, can be provided to serve this function. By "glass transition temperature" is meant the second order phase transition temperature as determined
35 empirically by mechanical methods as torsional braid analysis and the like or as calculated from monomer

composition by the method of Fox. By "effective glass transition temperature" is meant the second order phase transition temperature of the polymeric material as modified by the presence of low molecular weight species such as coalescents, solvent, and the like. The function of the selected polymeric latex in contrast is to improve the opacity of the film formed by the polymeric binder latex and the titanium dioxide pigment particles. To serve this function, it may be desirable that the selected polymeric latex particles be relatively rigid, having a relatively high effective glass transition temperature under the application conditions, for example, at least about 20 °C, more preferably at least about 35 °C, and even more preferably at least about 50 °C. Thus, one presently preferred embodiment of the present invention provides an aqueous mixture of the selected, opacity-improving "hard" polymeric latex particles and the non-selected, film-forming "soft" polymeric latex particles for use in preparing formulated aqueous compositions, such as coating compositions.

With regard to the average particle size or diameter of the selected polymeric latex particles and the titanium dioxide pigment particles employed in the present process, it is generally preferred that the selected polymeric latex particles have an average diameter of from about 20 nm to about four times that of the titanium dioxide pigment particles, and more preferably from about 20 nm to about the same diameter as that of the titanium dioxide pigment particles. In one presently preferred embodiment, in the case of selected "hard" polymeric latex particles, an average polymer latex diameter from about 30 nm to about 100 nm is preferred, and an average polymer latex diameter from about 50 nm to 80 nm is especially preferred.

In a second presently preferred embodiment, in the case of selected "soft" polymeric latex particles, an average polymeric latex particle diameter of from about 80

nm to 600 nm is preferred, and an average particle diameter of from about 100 nm to 400 nm is especially preferred. In at least some coating compositions, hiding is maximized when the selected polymeric latex particle diameter is greater than the titanium dioxide particle diameter.

The concentration of the titanium dioxide particles (and any other pigments which may be present in the composition) in a coating formulation is expressed in terms of the pigment volume concentration of the formulation. The pigment volume concentration (hereinafter referred to as the "PVC") of a formulation is defined as the volume amount of inorganic particles, including titanium dioxide and other pigment particles as well as extender particles, present in the formulation, divided by the sum of the volume amount of such inorganic particles plus polymeric latex particle solids in the formulation. Preferably, the PVC of compositions prepared according to the present invention is from about 5 to 60, and more preferably from about 10 to 50.

The overall concentration of pigment particles, extender particles and emulsion polymer particles in a formulation is typically expressed in terms of a percent volume solids for the formulation. The percent volume solids is an expression of the extent of the dilution of the solids in a liquid vehicle, such as water.

The polymeric latexes used in the practice of the present invention can have monomer compositions and particle sizes closely related to polymeric latex binders prepared by standard emulsion polymerization techniques known in the art.

In a presently preferred embodiment of the process of the present invention, the selected polymeric latex particles do not themselves provide a binder for the product formed by the fully formulated aqueous composition. Because they are not required to flow and form a film, the particles can be more rigid than those employed to provide a binder. Thus, the polymeric particles can have a higher effective

glass transition temperature than polymeric particles employed to serve as binder, and/or can include rigidifying levels of crosslinking. In this case the polymeric latex can also be prepared by standard emulsion polymerization techniques, but typically will not be suitable for use as a film-forming binder.

The selected polymeric latex particles useful in the process of this invention may be prepared by several alternative processes. In one such process, emulsion polymerization process variables are controlled to provide a water-insoluble polymer latex in which the total weight of ethylenically unsaturated acid-functional monomer preferably comprises at least about ten percent by weight of the polymeric latex solids. In another such process, the polymeric latex is prepared from monomer in which itaconic acid comprises more than one percent by weight.

In still another process for preparing the selected polymeric latex particles, the monomer mixture from which the polymeric latex is polymerized includes at least one dihydrogen phosphate ester of an alcohol in which the alcohol contains a polymerizable olefinic group, such as a polymerizable vinyl group. Examples of such dihydrogen phosphate esters include allyl phosphate, allyl cellosolve phosphate, hydroxyethyl methacrylate phosphate, the mono- or diphosphate of bis(hydroxyethyl) fumarate or itaconate, etc. In particular, polymeric latex particles polymerized from monomer mixtures including the dihydrogen phosphate ester of 2-hydroxyethyl methacrylate are preferred.

Without intending to be bound by any particular explanation of the mechanism of the process of the present invention, it is presently believed that selected polymeric latexes having acidic functionality with a pKa intermediate between weak and strong acids can be effective in the process of the present invention, such as those polymerized from monomer including copolymerizable, ethylenically unsaturated monomers with acidic functional groups with a

pKa from about 4 to 8, more preferably about 6. It should be noted that the pKa of an acidic functional group can vary depending upon its environment. For example, the measured pKa of an acid functional group can change when a polymerizable monomer bearing that group is copolymerized with more hydrophobic comonomers and the environment of the acid functional group becomes more hydrophobic. It is theorized that the pKa of the acidic functionality of the selected polymeric latex must be high enough that a significant proportion of these acidic functionalities are converted to their conjugate base form under basic conditions such as are frequently employed in aqueous polymeric latex-based coating compositions. It is further theorized that the pKa of the acidic functionality of the selected polymeric latex must not be so high that its conjugate base form is too weak a base.

Thus, the present invention provides aqueous dispersions, coating compositions, and pigment slurries including selected polymeric latex particles and titanium dioxide pigment particles, selected polymeric latex particles including, for example, dihydrogen phosphate ester functional groups.

These dihydrogen phosphate ester functional groups are believed to result from the polymeric latex particles being polymerized from monomer including at least one polymerizable dihydrogen phosphate-functional monomer. The polymerizable dihydrogen phosphate-functional monomer can be selected from the dihydrogen phosphate esters of an alcohol, the alcohol including a polymerizable group selected from polymerizable vinyl groups and polymerizable non-vinyl olefinic groups. The polymerizable dihydrogen phosphate-functional monomer can be selected from the dihydrogen phosphate monoester of 2-hydroxyethyl methacrylate, and mixtures of the dihydrogen phosphate monoester of 2-hydroxyethyl methacrylate and the phosphoric acid diester of 2-hydroxyethyl methacrylate.

Similarly, the present invention provides aqueous dispersion, coating compositions, and pigment slurries including selected polymeric latex particles and titanium dioxide pigment particles, the selected polymeric latex particles including polymerized residues of itaconic acid.

The polymeric latex used in the present invention can be prepared by any technique known in the art, such as suspension polymerization or emulsion polymerization. Emulsion polymerization techniques for preparing aqueous dispersions of latex polymer particles from ethylenically unsaturated monomers are well known in the polymer arts, and any conventional emulsion technique can be used, such as single and multiple shot batch processes, and continuous processes. If desired, a monomer mixture can be prepared and added gradually to the polymerization vessel. The monomer composition within the polymerization vessel can be varied during the course of the polymerization, such as by altering the composition of the monomer being fed into the vessel. Both single and multiple stage polymerization techniques can be used. The latex polymer particles can be prepared using a seed polymer emulsion to control the number of particles produced by the emulsion polymerization as is known in the art. The particle size of the latex polymer particles can be controlled by adjusting the initial surfactant charge as is known in the art. The preparation of polymeric latexes is discussed generally in D.C. Blackley, Emulsion Polymerization (Wiley, New York, 1975). The preparation of acrylic polymeric latexes is described in, for example, Emulsion Polymerization of Acrylic Polymers, Bulletin, Rohm and Haas Company, Philadelphia.

A polymerization initiator can be used in carrying out the polymerization of the polymeric latex particles. Examples of polymerization initiators which can be employed include polymerization initiators which thermally decompose at the polymerization temperature to generate free radicals. Examples include both water-soluble and water-insoluble

species. Examples of free radical-generating initiators which can be used include persulfates, such as ammonium or alkali metal (potassium, sodium or lithium) persulfate; azo compounds such as 2,2'-azo-bis(isobutyronitrile),
5 2,2'-azo-bis(2,4-dimethylvaleronitrile), and 1-t-butyl-azocyanocyclohexane); hydroperoxides such as t-butyl hydroperoxide and cumene hydroperoxide; peroxides such as benzoyl peroxide, caprylyl peroxide, di-t-butyl peroxide, ethyl 3,3'-di-(t-butylperoxy) butyrate, ethyl
10 3,3'-di(t-amylperoxy) butyrate, t-amylperoxy-2-ethyl hexanoate, and t-butylperoxy pivalate; peresters such as t-butyl peracetate, t-butyl perphthalate, and t-butyl perbenzoate; as well as percarbonates, such as di(1cyano-1-methylethyl)peroxy dicarbonate; perphosphates,
15 and the like.

Polymerization initiators can be used alone or as the oxidizing component of a redox system, which also includes a reducing component such as ascorbic acid, malic acid, glycolic acid, oxalic acid, lactic acid, thioglycolic acid,
20 or an alkali metal sulfite, more specifically a hydrosulfite, hyposulfite or metabisulfite, such as sodium hydrosulfite, potassium hyposulfite and potassium metabisulfite, or sodium formaldehyde sulfoxylate. The reducing component is frequently referred to as an
25 accelerator.

The initiator and accelerator, commonly referred to as catalyst, catalyst system or redox system, can be used in proportion from about 0.001% to 5% each, based on the weight of monomers to be copolymerized. Accelerators such as
30 chloride and sulfate salts of cobalt, iron, nickel or copper can be used in small amounts. Examples of redox catalyst systems include tertbutyl hydroperoxide/sodium formaldehyde sulfoxylate/Fe(II), and ammonium persulfate/sodium bisulfite/sodium hydrosulfite/Fe(II). The polymerization
35 temperature can be from room temperature to about 90 °C, and can be optimized for the catalyst system employed, as is

conventional.

Chain transfer agents can be used to control polymer molecular weight, if desired. examples of chain transfer agents include mercaptans, polymercaptans and polyhalogen compounds. Examples of chain transfer agents which may be used include alkyl mercaptans such as ethyl mercaptan, n-propyl mercaptan, n-butyl mercaptan, isobutyl mercaptan, t-butyl mercaptan, n-amyl mercaptan, isoamyl mercaptan, t-amyl mercaptan, n-hexyl mercaptan, cyclohexyl mercaptan, n-octyl mercaptan, n-decyl mercaptan, n-dodecyl mercaptan; alcohols such as isopropanol, isobutanol, lauryl alcohol and t-octyl alcohol; halogenated compounds such as carbon tetrachloride, tetrachloroethylene, and trichlorobromoethane. Generally from 0 to 10% by weight, based on the weight of the monomer mixture, can be used. The polymer molecular weight can be controlled by other techniques known in the art, such as selecting the ratio of initiator to monomer.

Catalyst and/or chain transfer agent can be dissolved or dispersed in separate or the same fluid medium and gradually added to the polymerization vessel. Monomer, either neat or dissolved or dispersed in a fluid medium, can be added simultaneously with the catalyst and/or the chain transfer agent. Amounts of initiator or catalyst can be added to the polymerization mixture to "chase" residual monomer after polymerization has been substantially completed to polymerize the residual monomer as is well known in the polymerization arts.

Aggregation of polymeric latex particles is typically discouraged by including a stabilizing surfactant in the polymerization mix. In general, the growing latex particles are stabilized during emulsion polymerization by one or more surfactants such as an anionic or nonionic surfactant, or a mixture thereof, as is well known in the polymerization art. Many examples of surfactants suitable for emulsion polymerization are given in McCutcheon's Detergents and

Emulsifiers (MC Publishing Co., Glen Rock, NJ), published annually. Other types of stabilizing agents, such as protective colloids, can also be used. However, it is preferred that the amount and type of stabilizing surfactant or other type of stabilizing agent employed during the polymerization reaction be selected so that residual stabilizing agent in the aqueous product of the polymerization reaction does not significantly interfere with the subsequent opacity improvement of the process of the present invention. Further, charged initiator fragments and copolymerized monomer bearing charged functional groups such as copolymerized acid-functional monomers are known to contribute to the stability of the resulting polymeric latex particles. It is important to note that stabilizing surfactants, copolymerized acidic monomers, residual initiator fragments, and the like, may also interfere with the subsequent opacity improvement of the process of the present invention. Thus adjusting polymerization conditions to provide a desired level of residual initiator fragments and surface acid may be very important in providing polymeric latex particles for use in the process of the present invention.

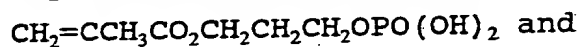
The polymeric latexes useful in the process of the present invention can be prepared from a wide range of polymerizable monomers, such as, for example, monoethylenically unsaturated monomers, including alpha, beta-monoethylenically unsaturated monomers such as alkyl acrylates and methacrylates. By "acrylic polymeric latex" is meant a polymeric latex polymerized from monomers comprising substantially polymerizable monomers including the acryl group ($-\text{COCH}=\text{CH}_2$) or methacryl ($-\text{COC}(\text{CH}_3)=\text{CH}_2$) group, and specifically greater than about 80 weight percent (meth)acrylic monomers, based on the total monomer weight. Mixtures of polymeric latexes can also be used.

Examples of polymeric latexes which can be employed in the process of the present invention include those

polymerized from ethylenically unsaturated monomers, such as alpha, beta -ethylenically unsaturated monomers, including styrene, butadiene, alpha-methylstyrene, vinyltoluene, vinylnaphthalene, ethylene, vinyl acetate, vinyl versatate, vinyl chloride, vinylidene chloride, acrylonitrile, methacrylonitrile, (meth)acrylamide, various (C1-C20)alkyl esters of (meth)acrylic acid; for example, methyl (meth)acrylate, ethyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)actylate, 2-ethylhexyl (meth)acrylate, cyclohexyl (meth)acrylate, n-octyl (meth)acrylate, n-decyl (meth)acrylate, n-dodecyl (meth)acrylate, tetradecyl (meth)acrylate, n-amyl (meth)acrylate, neopentyl (meth)acrylate, cyclopentyl (meth)acrylate, lauryl (meth)acrylate, oleyl (meth)acrylate, palmityl (meth)acrylate, and stearyl (meth)acrylate; other (meth)acrylates such as isobornyl (meth)acrylate, benzyl (meth)acrylate, phenyl (meth)acrylate, 2-bromoethyl (meth)acrylate, 2-phenylethyl (meth)acrylate, and 1-naphthyl (meth)acrylate; alkoxyalkyl (meth)acrylate such as ethoxyethyl (meth)acrylate; mono-, di-, and trialkyl esters of ethylenically unsaturated diand tricarboxylic acids and anhydrides, such as ethyl maleate, dimethyl fumarate, trimethyl aconitate, and ethyl methyl itaconate. As used in the present specification and claims, "(meth)acrylate" denotes both "acrylate" and "methacrylate" and "(meth)acrylic" denotes both "methacrylic" and "acrylic." The ethylenically unsaturated monomer can also include at least one multi-ethylenically unsaturated monomer effective to raise the molecular weight and crosslink the polymer. Examples of multiethylenically unsaturated monomers that can be used include allyl (meth)acrylate, tripropylene glycol di(meth)acrylate, diethylene glycol di(meth)acrylate, ethylene glycol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, 1,3-butylene glycol (meth)acrylate, polyalkylene glycol di(meth)acrylate, diallyl phthalate, trimethylolpropane tri(meth)acrylate,

divinylbenzene, divinyltoluene, trivinylbenzene, and divinylnaphthalene.

In addition to those monomers which are "functional" in the sense of including one or more polymerizable ethylenically unsaturated groups, monomers which also include one or more additional functional groups can be used in preparing the polymeric latexes used in the process of this invention. An important class of these functional monomers is that made up of those polymerizable ethylenically unsaturated monomers having acidic functional groups. Examples of these include acrylic acid, methacrylic acid, beta-acryloxypropionic acid and higher monoacidic oligomers of acrylic acid, ethacrylic acid, alpha chloroacetic acid, alpha-vinylacrylic acid, crotonic acid, alpha-phenylacrylic acid, cinnamic acid, chlorocinnamic acid, beta-styrylacrylic acid, itaconic acid, maleic acid, dihydrogen phosphate esters of an alcohol in which the alcohol also contains a polymerizable vinyl or olefinic group, such as allyl phosphate, allyl Cellosolve phosphate, mono- or diphosphate of bis(hydroxy-methyl) fumarate or itaconate, derivatives of (meth)acrylic acid esters, such as, for example, phosphates of hydroxyalkyl(meth)acrylates including 2-hydroxyethyl (meth)acrylate, such as Kayamer® (trademark of Nihon Kayaku Co., Ltd.) PM-1, PM-2, PA-1, and PA-2 monomers, 3-hydroxypropyl (meth)acrylates, and the like. Examples of dihydrogen phosphate ester derivatives which can be employed include vinylbenzyl phosphates, and:



Thus, the present invention also provides aqueous dispersions, coating compositions, and pigment slurries including selected polymeric latex particles and titanium dioxide pigment particles, in which the selected polymeric latex particles are polymerized from monomer including at

least one polymerizable dihydrogen phosphate-functional monomer selected from the dihydrogen vinylbenzyl phosphates, and $\text{CH}=\text{CCH}_3\text{CO}_2\text{CH}_2\text{CH}_2\text{OPO}(\text{OH})_2$, $\text{CH}_2=\text{CCH}_3\text{CO}_2\text{CH}_2\text{CH}[\text{OPO}(\text{OH})_2]\text{CH}_3$, $\text{CH}_2=\text{CCH}_3\text{CO}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OPO}(\text{OH})_2$ and $\text{CH}_2=\text{CCH}_3\text{CO}_2\text{CH}_2\text{CHOHCH}_2\text{OPO}(\text{OH})_2$.

5 Small amounts of acid-functional copolymerizable monomer, such as methacrylic acid and/or acrylic acid, are typically included in preparing polymeric latexes to confer colloidal stability. As noted above, in one embodiment of the present invention, preparation of the polymeric latex
10 particles from monomer mixture including greater than one percent by weight itaconic acid is preferred. In another preferred embodiment, a relatively large amount of acid-functional copolymerizable monomer, such as methacrylic acid, for example, at least about five percent by weight of
15 total polymer solids, and preferably at least about ten percent by weight of total polymer solids, is included in the monomer mix, and a process which provides water-insoluble polymeric latex particles is employed. In yet another presently preferred embodiment of the present
20 invention, as noted above, the polymeric latex employed is polymerized from monomer mixture including at least one phosphoric acid partial ester derivative of a (meth)acrylic acid ester, preferably including a dihydrogen phosphate monoester. Other types of copolymerizable functional
25 monomers can also be included, depending on the ultimate application for which the product produced by the process of the present invention is intended. For example, small amounts of adhesion-promoting copolymerizable monomers can also be included. Examples of other types of functional
30 monomers include hydroxy-functional monomers such as 2-hydroxethyl (meth)acrylate, amino-functional monomers such as dimethylaminoethyl (meth)acrylate, epoxy-functional monomers, such as glycidyl methacrylate and the like. Examples of synthetic polymeric latexes which can be used
35 include acrylic copolymer latexes, such as butyl acrylate/methyl methacrylate/acid and ethyl acrylate/methyl

include acrylic copolymer latexes, such as butyl acrylate/methyl methacrylate/acid and ethyl acrylate/methyl methacrylate/acid copolymer latexes; vinyl acetate homopolymer and copolymer latexes, including ethylene/vinyl acetate copolymer latexes; styrene/butadiene copolymer latexes; and the like.

By selecting the type and concentration of monomers having known glass transition temperatures and acid functionalities, polymeric latexes having properties useful in the process of the invention can be prepared.

The particle size, particle size distribution, and molecular weight of the polymeric latex can be selected by the choice of a particular polymerization process, as for example through the use of particular initiator and chain transfer systems, as is well known in the polymerization arts. The average particle size and the molecular weight of the polymeric latex are important with regard to both the opacity improvement, as well as with respect to the properties of the polymeric latex when it is employed as a binder in the fully formulated aqueous composition.

Preferably, the selected polymeric latex used in the process of the present invention has an average particle diameter in the range of from approximately four times the average particle diameter of the titanium dioxide pigment particles down to about 20 nm. For example, if the titanium dioxide particles to be used have an average particle size of about 200 nanometers, the polymeric latex particle should have an average particle size in the range of from about 20 to less than about 800 nanometers. By "average particle size" or "average particle diameter" is meant an average determined experimentally by the quasielastic light scattering technique, such as provided, for example, by the Model BI-90 Particle Sizer, of Brookhaven Instruments Corp.

The titanium dioxide particles, can be pretreated to provide inorganic surface coatings, such as coatings of silica, aluminum oxide, or mixtures of silica and aluminum

oxide, on titanium dioxide particles. In addition, small molecular species, such as silanes or titanates, can be adsorbed on and reacted with surface of the titanium dioxide particles, and the resulting surface sites can be subsequently modified chemically. Examples of such species include N-2-aminoethyl-3-aminopropyltrimethoxysilane, 3-aminopropyltrimethoxysilane, 3-methacryloxypropyltrimethoxysilane, and vinyltriacetoxysilane. Alternatively, other species can be simply adsorbed to the surface of the titanium dioxide pigment particles. The most important examples of these are low molecular weight polyelectrolytes such as conventional pigment dispersants.

Examples of suitable anionic polyelectrolyte pigment dispersants for use in the process of the present invention include polyacrylic acid, polymethacrylic acid, copolymeric acids including copolymerized maleic acid, polyphosphates such as potassium tripolyphosphate, and the like.

While the chemical composition of a polymeric latex binder is important for achieving the resultant properties of the coating or film when the polymeric latex also acts as the binder, the glass transition temperature and amount of acid functionality in the polymeric latex can also be important for the purpose of the invention. Hard polymeric latex particles, preferably having an average particle diameter of from about 50 nm to 80 nm, are preferred in one embodiment of this invention. Soft polymeric latex particles preferably having a particle diameter of from about 100 nm to about 400 nm are preferred in another embodiment.

The presence of conventional polyelectrolyte dispersants has a significant effect on the opacity improvement of the present invention. While low concentrations of conventional water-soluble polyelectrolyte dispersants, on the order of about 0.2 weight percent or lower, have little adverse effect on the opacity improvement, the use of higher concentrations of these

conventional water-soluble polyelectrolytes dispersants can have a significant adverse effect upon opacity unless the polymeric latex is carefully selected.

In some cases, it is possible to practice the process of the present invention without employing a pigment dispersant to disperse the titanium dioxide pigment particles, although it is generally preferred that a pigment dispersant be used.

In one presently preferred embodiment of the present invention an emulsion polymerization process is used to prepare a polymeric latex from monomer mixture including one or more ethylenically polymerizable derivatives of phosphoric acid, such as one or more partial esters of phosphoric acid and 2-hydroxy-ethyl methacrylate. Examples of such partial esters are given above and include the monoester of phosphoric acid with hydroxyethyl methacrylate, the diester of phosphoric acid with hydroxyethyl methacrylate, and mixture thereof. The resulting phosphoric acid ester-functional polymeric latex particles result in improved opacity compared to polymeric latex prepared from monomer mixture which does not include phosphoric acid ester-functional monomer.

The process of the present invention can significantly increase the hiding of titanium dioxide containing emulsion paint formulations (as determined by measuring the scattering coefficient of the paint) of the same PVC compared with the scattering coefficient of a paint formulation prepared by the use of conventional polymeric latices. An alternate way of expressing this improvement is that the process of the invention permits the reduction of the PVC of a 20% PVC titanium dioxide paint formulation by 20 percent while achieving the same scattering coefficient or degree of hiding as can be obtained by the use of a conventional polymeric latex.

Furthermore, the improved performance of paint formulations prepared by the present process is achieved

even in the presence of substantial amounts of large particle size extenders, such as calcium carbonate and alumino silicate, typically employed in such formulations.

In addition, the improved hiding achievable by use of the process of this invention is realized when the coating formulation is prepared with conventional thickeners of the associative and non-associative types; this improvement is not dependent upon the selected thickener. This result is surprising and contrary to the result typically encountered when paints are formulated using conventional polymeric latices. In such conventional systems the hiding property of the formulated paint can vary greatly as a function of the thickener employed. The process of the invention therefore offers paint formulators a greater choice in selecting thickeners for the final paint formulation without concern over the choice of thickener adversely affecting the final hiding properties of the paint.

Furthermore, in addition to improving the hiding of paint formulations, the process of this invention also has been found to advantageously improve the early blister resistance, metal marking resistance, gloss, high shear viscosity, and scrub resistance of paint formulations compared with paint formulations prepared with conventional polymeric latices, as well as improving the corrosion resistance of paint formulations.

In addition to the titanium dioxide particles, which are typically of relatively small particle size, on the order of 200-250 nm, other pigment particles, such as the large particle size extender pigment particle typically included in many types of coating formulation to reduce new material costs, can also be employed in addition to the titanium dioxide pigment particles in the process of the present invention. Examples of large particle size extender pigment particles which can be used include calcium carbonate, alumino-silicate, amorphous silicon, and the like.

Similarly, the aqueous medium in which the titanium dioxide particles are ground with the polymeric latex dispersant can also include water-miscible solvents, such as glycols and glycol ethers, such as are conventional in the coatings arts. Examples of water-miscible solvents employed include propylene glycol, ethylene glycol, ethylene glycol monomethyl ether, and the like.

Aqueous coating compositions are frequently formulated at alkaline pH to stabilize anionically charged latex binder against agglomeration and for other reasons. The principles of formulating aqueous coating compositions are reviewed, for example, in Formulation of Organic Coatings (N.I. Gaynes ed. D. Van Nostrad Co. Inc. Princeton, NJ 1967) at pp. 189-230.

The present invention provides aqueous dispersions including selected polymeric latex particles and titanium dioxide pigment particles, which can be used in a variety of applications. In some cases, a "soft" (i.e. low effective glass transition temperature, such as on the order of 0 °C to 10 °C) polymeric latex can be added to the dispersion, typically with the further addition of other components, the soft polymeric latex serving as binder for the composition. Often the binder-forming latex polymer particles contain carboxyl functional groups. Under suitable conditions, the carboxyl groups are ionized and the resultant charges on the latex particle surface electrostatically stabilize the latex against premature agglomeration. Often a volatile base, typically ammonia, is used to adjust the pH of the coating composition. When the coating composition is applied to a substrate to be coated, the volatile base is lost and the pH of the coating composition drops, destabilizing the latex particles of the binder and thus encouraging agglomeration to form a continuous binder film.

In addition to binder-forming polymeric latex particles, selected polymeric latex particles, and titanium dioxide pigment particles, aqueous coating compositions

prepared according to the process of the present invention can include typical coatings ingredients. For example, they can include extender pigments as noted above such as calcium carbonate, amorphous silica, and the like; defoamers; 5 biocidal agents such as zinc oxide, 2-N-octyl-4-isothiazole-3-one, and phenyl mercuric acetate; coalescing agents such as diethylene glycol monoethyl ether acetate and ethylene glycol monobutyl ether acetate; plasticizers such as dialkyl phthalates including dibutyl 10 phthalate, dioctyl phthalate and the like; freeze-thaw stabilizers such as ethylene glycol, propylene glycol and diethylene glycol; nonionic wetting agents such as polyethylenoxylates of fatty acids, alkanols, alkylphenols, and glycols; polyelectrolyte pigment dispersants; thickeners 15 such as polyelectrolyte and cellulosic thickeners; rheology control agents such as associative thickeners and the like; colorants such as colored pigments and dyes; perfumes; cosolvents and the like.

The illustrative examples which follow illustrate the 20 process of the present invention as a function of the parameters of the selected emulsion polymer. These examples will aid those skilled in the art in understanding the present invention; however, the present invention is in no way limited thereby. In the examples which follow, 25 percentage composition is by weight, unless otherwise noted.

Examples 1 - 2

A typical conventional 20% PVC gloss paint 30 (Comparative Example 1) was prepared according to the following formulation.

Pigment grind:

24

	<u>Components</u>	<u>Weight (g)</u>
	water	30
	propylene glycol	20
	Colloid 643 defoamer	1
5	Tamol® 731 dispersant (25% solids)	8.19
	Ti-Pure® R-900 titanium dioxide	204.72

Tamol 731 is a polycarboxylate dispersant (Tamol is a trademark of Rohm and Haas Company). Tamol 731 is a sodium salt of polymeric carboxylic acid. Ti-Pure is a trademark of Du Pont de Nemours Co. Ti-Pure R-900 is a coatings grade of rutile titanium dioxide. These components were milled on a high speed disk disperser to form a pigment grind, and were let down at a slower speed with the following:

	<u>Components</u>	<u>Weight (g)</u>
	Rhoplex® AC-61 polymer latex	493.75
	Colloid 643 defoamer	4
	Texanol® coalescent	22.96
20	Triton® GR-7M surfactant	2
	propylene glycol	59
	Nuosept® 95 preservative	6
	water and Natrosol® 250 MR	165.07
	cellulosic thickener	

Rhoplex is a trademark of Rohm and Haas Company. Texanol is a trademark of Eastman Kodak Co. Triton is a trademark of Rohm and Haas Company. Nuosept is a trademark of Nuodex, Inc. The mix is thickened to a Stormer viscosity of 80 KU by addition of an aqueous solution of the cellulosic thickener, and the pH of the mix is adjusted to 9 by addition of ammonia.

To provide Example 1, the paint formulation process of Comparative Example 1 was repeated replacing the 493.75 g of Rhoplex AC-61 with a mixture of 419.66 g Rhoplex AC-61 (46.5% solids) and 92.04 g of a polymeric latex having a

glass transition temperature of 65 °C, a particle size of 71 nm, and having 6% phosphoethyl methacrylate (Latex A, 37.4% solids). The total weight of water was adjusted to maintain the same total solids in the final paint.

5 To provide Example 2, the paint formulation process of Example 1 was repeated replacing the 92.04 g of a polymeric Latex A with 94.26 g of a polymeric latex having a glass transition temperature of 90 °C, a particle size of 69 nm, and having 4% itaconic acid (Latex B, 36.5% solids).
10 The total weight of water was adjusted to maintain the same total solids in the final paints.

Kubleka-Munk scattering coefficients were determined for all paints using a modification of ASTM D 2805-70.

Results given in Table I.

15

Table I

	<u>Example</u>	<u>Dispersant</u>	<u>Binder</u>	<u>Scattering Coefficient</u>
20	Comp. 11	1% Tamol 731	AC-61	7.26
	1	1% Tamol 731	AC-61/Latex A	7.77
	2	1% Tamol 731	AC-61/Latex B	7.69

25

1. Comparative Example.

The results in Table I demonstrate that a polymeric latex with phosphoethyl methacrylate (Example 1) or itaconic
30 acid (Example 2) when blended with a conventional latex will result in improved opacity compared to a conventional latex alone as reflected by the Kubleka-Munk scattering coefficients.

35

Example 3

An acrylate polymeric latex emulsion was prepared having a calculated glass transition temperature of about 14 °C, a particle size of 161 nm, and total solids of about 45

percent by weight using a single-stage, gradual-addition thermal process from monomer including 1.3 percent by weight methacrylic acid and one percent by weight phosphoethyl methacrylate (Latex C). A pigment grind was prepared by grinding together at high speed 200 parts by weight TiPure R-900 titanium dioxide, 8 parts by weight Tamol 731 pigment dispersant, 1 part by weight Colloid 643 defoamer, 20 parts by weight propylene glycol and 30 parts by weight water. 495.6 parts by weight of Latex C were mixed at low speed with 7.57 parts by weight water and 22.64 parts by weight Texanol. Subsequently, to the Latex C/Texanol mixture were added 9.70 parts by weight Triton X-405 surfactant, 49.57 parts by weight water, 4 parts by weight Colloid 643 defoamer, 59 parts by weight propylene glycol, and 6 parts by weight Nuosept 95 preservative. To this mixture was added the grind, and subsequently, 100.4 parts by weight of a 5.0 percent by weight solution of Natrosol 250 MR hydroxycellulose thickener were added to provide a paint (Example 3) with a PVC of 20, a calculated volume solids of 32 percent, and a calculated weight solids of 42.1 percent. The hiding and gloss of the paint were evaluated and compared with a control paint prepared from an polymeric latex made using a similar process but omitting the phosphoethyl methacrylate (Comparative Example 2), the results being given in Table III, and showing improved hiding and gloss using the process of the present invention.

Table II

	<u>Example</u>	<u>Hiding</u>	<u>20' Gloss</u>	<u>60' Gloss</u>
30	Comp. 21	6.9	14	54
	3	7.8	24	63

1. Comparative example

Example 4

To 1300 g of deionized water stirred under a nitrogen atmosphere at 85°C was added 4 g of ammonium persulfate in 24 g of deionized water and 60 g of a seed latex. A monomer emulsion prepared from 600 g of deionized water, 28 g of Siponate DS-4, 900 g of butyl acrylate, 876.6 g of methyl methacrylate and 23.4 g of methacrylic acid was added over a 200-min period along with 2 g of ammonium persulfate in 100 g of deionized water maintaining 85°C. When the reaction was complete, the dispersion was cooled and filtered. The product (Latex D) had 45.6% solids and pH 3 with an average diameter of 196 nm.

The process used to prepare Latex D was repeated, except that 18 g of the methyl methacrylate was replaced with an equal weight of Kayamer (trademark of Nihon Kayaku Co. Ltd.) PM-1 (monomer mixture containing around 52% of the monoester of hydroxyethyl methacrylate and phosphoric acid and 33% of the diester). The product (Latex E) had 46.1% solids and pH 2.6 with an average particle size of 185 nm.

A tinted titanium dioxide dispersion was prepared from 180 g of deionized water, 7.2 g of Tamol 731 dispersant (25% solids), 3.0 g of Nopco NXZ defoamer, 600 g of Ti-Pure R-902 and 30 g of Colortrend lamp black dispersion. Samples of Latex D and Latex E were adjusted to pH 9 with 28% aqueous ammonia and used to formulate paints with 14% volume concentration of Ti-Pure R-902 pigment in the dry paint: To 29.5 g of R-902 dispersion was added 7.8 g of water, 83.9 g of the pH 9 Latex D, 2.6 g of Texanol coalescent, 7.2 g of propylene glycol and 24.0 g of 2.5% aqueous Natrosol 250 MR hydroxyethyl cellulose thickener. Latex E was formulated similarly only 82.8 g were required and 8.9 g of water. The two paints were allowed to equilibrate for seven days and then their Y-reflectance was measured using a 45°/0° reflectometer (Colorguard, Gardner Instruments). From light scattering theory, the ratio of the scattering coefficient,

S, and the adsorption coefficient, K, is given by:

$$S/K = 2R/(1-R)^2$$

5 where R is the reflectance from an infinitely thick layer of dry paint film. At a given titanium dioxide PVC, differences in Y-reflectance of equally tinted paint films arise solely from differences in titanium dioxide scattering efficiency. Titanium dioxide dominates the scattering while
10 the tinting agent dominates the adsorption which can then be considered constant. The percentage difference in scattering coefficient exhibited by two equally tinted paints is then given by:

$$((S_2 - S_1)/S_1) \times 100 = ((R_2(1 - R_1)^2/R_1(1 - R_2)^2) - 1) \times 100$$

15

Results are given in Table III.

<u>Table III</u>		
<u>Example</u>	<u>Latex</u>	<u>Y-Reflectance</u>
20 Comp. 31	D	0.504
4	E	0.540

1. Comparative example.

These results show that the phosphate-containing
25 binder (Latex E) results in increased Y-reflectance compared to standard binder (Latex D) corresponding to an increase in scattering efficiency of the titanium dioxide in the dry paint film of 25%.

Various modifications can be made in the details of
30 the various embodiments of the compositions and processes of the present invention, all within the spirit and scope of the invention as defined by the appended claims.

CLAIMS

1. A process for preparing an aqueous dispersion including selected polymeric latex particles and titanium dioxide pigment particles, the process comprising:

a) dispersing titanium dioxide pigment particles in an aqueous medium;

b) preparing a dispersion or suspension of selected polymeric latex particles in the aqueous medium, the polymeric latex particles being prepared by an emulsion polymerization process, the emulsion polymerization process being selected from the class consisting of:

1) emulsion polymerization processes employing a monomer mixture including at least one polymerizable ethylenically unsaturated acid-functional monomer, the at least one polymerizable ethylenically unsaturated acid-functional monomer being selected from the class consisting of:

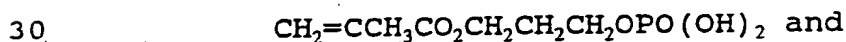
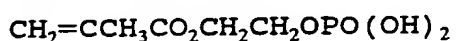
the phosphoric acid monoester of 2-hydroxyethyl methacrylate,

the phosphoric acid diester of 2-hydroxyethyl methacrylate,

the phosphoric acid monoester of 3-hydroxypropyl methacrylate,

and the phosphoric acid diester of 3-hydroxypropyl methacrylate,

the dihydrogen vinylbenzylphosphates,



2) emulsion polymerization processes providing polymeric latex particle polymerized from monomer including more than one percent by weight itaconic acid; and

3) emulsion polymerization processes employing a monomer mixture including at least one ethylenically unsaturated acid-functional monomer, the total weight of

ethylenically unsaturated acid-functional monomer comprising at least about ten percent by weight of the polymeric latex solids; and

5 c) mixing the aqueous medium containing the titanium dioxide pigment particles and the selected polymeric latex particles.

2. A process according to claim 1 wherein the titanium dioxide pigment particles are dispersed in the aqueous medium by employing a pigment dispersant.

10 3. A process according to claim 2 wherein the pigment dispersant is a polyelectrolyte.

4. A process according to claim 3 wherein the pigment dispersant is selected from poly(meth)acrylic acid, poly(meth)acrylic acid salts, polyelectrolyte copolymers of 15 (meth)acrylic acid and salts of polyelectrolyte copolymers of (meth)acrylic acid and their salts.

5. A process according to claim 3 wherein the pigment dispersant is an inorganic polyelectrolyte.

20 6. A process according to claim 5 wherein the pigment dispersant is a polyphosphate salt.

7. A process according to claim 2 wherein the selected polymeric latex has an effective glass transition temperature greater than about 20 °C.

25 8. A process according to claim 7 wherein the selected polymeric latex has an effective glass transition temperature greater than about 50 °C.

9. A process according to claim 2 wherein the average size of the polymeric latex particles is from about 20 nm to about four times the average particle size of the titanium 30 dioxide pigment particles.

10. A process according to claim 9 wherein the average size of the polymeric latex particles is from about one-half the average size of the titanium dioxide pigment particles to about equal to the average size of the titanium dioxide 35 pigment particles.

11. A process according to claim 2 wherein the average

particle size of the titanium dioxide pigment particles is from about 100 nm to 10,000 nm, and the average size of the polymeric latex particles is from about 20 nm to 5000 nm.

12. A process according to claim 11 wherein the average
5 particle size of the titanium dioxide pigment particles is from about 200 nm to 250 nm, and the average size of the polymeric latex particles is from about 20 nm to 1000 nm.

13. A process according to claim 2 wherein the
10 effective glass transition temperature of the selected polymeric latex is less than about 20 °C, the average particle size of the selected polymeric latex being from about 80 nm to 600 nm.

14. A process according to claim 13 wherein the average
15 particle size of the selected polymeric latex is from about 100 nm to 400 nm.

15. A process according to claim 1 wherein the average
particle size of the polymeric latex particles is from about 30 nm and 100 nm.

16. A process according to claim 15 wherein the average
20 particle size of the polymeric latex particles is from about 50 nm to 80 nm.

17. A process according to claim 2 further comprising
mixing an aqueous dispersion of polymeric latex binder
particles with the aqueous dispersion including selected
25 polymeric latex particles and titanium dioxide pigment particles.

18. A coating composition produced according to the
process of claim 2.

19. A coating composition according to claim 18 having
30 a PVC from about 5 to 60.

20. A coating composition according to claim 19 having
a PVC from about 10 to 50.

21. An aqueous dispersion including polymeric latex and
titanium dioxide pigment, the polymeric latex including
35 dihydrogen phosphate ester functional groups, the polymeric latex being polymerized from monomer including at least one

polymerizable dihydrogen phosphate-functional monomer
selected from the class consisting of:

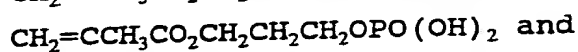
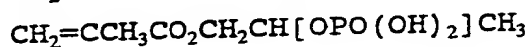
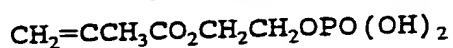
the phosphoric acid monoester of 2-hydroxyethyl
methacrylate,

5 the phosphoric acid diester of 2-hydroxyethyl
methacrylate,

the phosphoric acid monoester of 3-hydroxypropyl
methacrylate,

10 and the phosphoric acid diester of 3-hydroxypropyl
methacrylate,

the dihydrogen vinylbenzylphosphates,



15 $\text{CH}_2=\text{CCH}_3\text{CO}_2\text{CH}_2\text{CHOHCH}_2\text{OPO}(\text{OH})_2$.

22. A coating composition comprising an aqueous
dispersion including polymeric latex and titanium dioxide
pigment, the polymeric latex including dihydrogen phosphate
ester functional groups, the polymeric latex being
20 polymerized from monomer including at least one
polymerizable dihydrogen phosphate functional monomer
selected from the class consisting of:

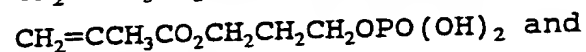
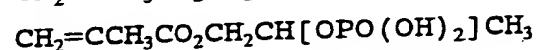
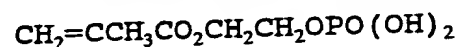
the phosphoric acid monoester of 2-hydroxyethyl
methacrylate,

25 the phosphoric acid diester of 2-hydroxyethyl
methacrylate,

the phosphoric acid monoester of 3-hydroxypropyl
methacrylate,

30 and the phosphoric acid diester of 3-hydroxypropyl
methacrylate,

the dihydrogen vinylbenzylphosphates,



35 $\text{CH}_2=\text{CCH}_3\text{CO}_2\text{CH}_2\text{CHOHCH}_2\text{OPO}(\text{OH})_2$.

23. A pigment slurry comprising an aqueous dispersion

including polymeric latex and titanium dioxide pigment, the polymeric latex and titanium dioxide pigment, the polymeric latex including dihydrogen phosphate ester functional groups, the poly-eric latex being polymerized from monomer including at least one polymerizable dihydrogen phosphate-functional monomer selected from the class consisting of:

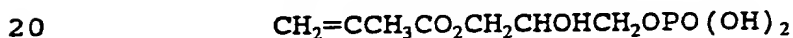
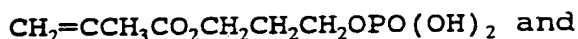
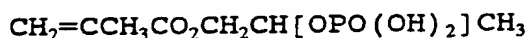
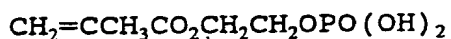
the phosphoric acid monoester of 2-hydroxyethyl methacrylate,

10 the phosphoric acid diester of 2-hydroxyethyl methacrylate,

the phosphoric acid monoester of 3-hydroxypropyl methacrylate,

15 and the phosphoric acid diester of 3-hydroxypropyl methacrylate,

the dihydrogen vinylbenzylphosphates,



24. An aqueous dispersion including polymer latex and titanium dioxide, the polymeric latex being polymerized from monomer including more than one percent by weight itaconic acid.

25 25. A coating composition comprising an aqueous dispersion including polymeric latex and titanium dioxide pigment, the polymeric latex being polymerized from monomer including more than one percent by weight itaconic acid.

26. A pigment slurry comprising an aqueous dispersion including polymeric latex and titanium dioxide pigment, the polymeric latex being polymerized from monomer including more than one percent by weight itaconic acid.

27. A coating composition comprising an aqueous dispersion including polymeric latex and titanium dioxide pigment, the coating composition having a PVC from about 5 to 60, the polymeric latex being prepared by an emulsion

polymerization process, the emulsion polymerization process being selected from the class consisting of:

1) emulsion polymerization processes employing a monomer mixture including at least one polymerizable ethylenically unsaturated acid-functional monomer, the at least one polymerizable ethylenically unsaturated acid-functional monomer being selected from the class consisting of:

A) itaconic acid, the total weight of itaconic acid in the monomer used for the polymerization being greater than one percent of the total weight of monomer, and

B) dihydrogen phosphate esters of an alcohol, the alcohol containing a polymerizable olefinic group; and

2) emulsion polymerization processes employing a monomer mixture including at least one ethylenically unsaturated acid-functional monomer and providing a water-insoluble polymeric latex, the total weight of ethylenically unsaturated acid-functional monomer comprising at least about ten percent by weight of the polymeric latex solids; and

c) mixing the aqueous medium containing the inorganic material particles and the selected polymeric latex particles, the selected polymeric latex particles adsorbing onto the inorganic material particles to provide the composite particles.

28. A coating composition according to claim 27 having a PVC from about 10 to 50.

29. A coating composition according to claim 27 wherein the average size of the polymeric latex particles is from about 20 nm to about four times the average particle size of the titanium dioxide pigment particles.

30. A coating composition according to claim 27 wherein the average size of the polymeric latex particles is from about one-half the average size of the titanium dioxide pigment particles to about equal to the average size of the titanium dioxide pigment particles.

31. A coating composition according to claim 27 wherein the average particle size of the titanium dioxide pigment particles is from about 100 nm to 10,000 nm, and the average size of the polymeric latex particles is from about 20 nm to 5000 nm.

32. A coating composition according to claim 31 wherein the average particle size of the titanium dioxide pigment particles is from about 200 nm to 250 nm, and the average size of the polymeric latex particles is from about 20 nm to 1000 nm.

33. A process for preparing an aqueous dispersion including selected polymeric latex particles and titanium dioxide pigment particles, the process comprising:

- a) dispersing titanium dioxide particles in an aqueous medium;
- b) preparing a dispersion or suspension of selected polymeric latex particles in the aqueous medium, the polymeric latex particles being prepared by an emulsion polymerization process employing a monomer mixture including at least one polymerizable ethylenically unsaturated acid-functional monomer selected from the class consisting of monobasic and polybasic monomers having acidic functional groups including at least one proton with an acid equilibrium constant such that the negative logarithm of the acid equilibrium constant (pKa) is from about 4 to 8; and
- c) mixing the aqueous medium containing the titanium dioxide particles and the selected polymeric latex particles.

34. A process according to claim 33 wherein the negative logarithm of acid equilibrium constant is about 6.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US92/09434**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(5) : ~~C08L 3/00~~; C08K 3/22, 9/00; C08L 33/00, 51/00, 41/00, 31/00
US CL : 523/205; 524/497, 522, 539, 547, 556, 559, 881
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 523/205; 524/497, 522, 539, 547, 556, 559, 881

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A, 4,102,843 (SPERRY ET AL.) 25 JULY 1978 see column 2, lines 12-14; column 3, lines 38-43; and column 4, lines 9, 10 and 39-40.	1-20 and 24-34
X	US,A, 4,421,660 (SOLC NEE HAJNA) 20 DECEMBER 1983 see columns 1-3.	1-20 and 24-34
Y	US,A, 4,110,285 (PONS ET AL.) 29 AUGUST 1978 see entire document	1-34
Y	US,A, 4,506,057 (GREENE ET AL.) 19 MARCH 1985 see entire document	1-34
X	US,A, 4,435,540 (KISHIDA ET AL.) 06 MARCH 1984 see columns 3 and 4.	1-20 and 24-34

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

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Date of the actual completion of the international search

28 DECEMBER 1992

Date of mailing of the international search report

11 MAR 1993

Name and mailing address of the ISA/
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Authorized officer

PATRICK NILAND

Facsimile No. NOT APPLICABLE

Telephone No. (703) 308-2351